



## Removal of NO<sub>x</sub> from air through cooperation of the TiO<sub>2</sub> photocatalyst and urea on activated carbon fiber at room temperature

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### ABSTRACT

Removal of atmospheric NO to harmless N<sub>2</sub> was successfully achieved through the continuous oxidation and reduction of NO into N<sub>2</sub> using pitch-based activated carbon fiber (ACF), in which TiO<sub>2</sub> and urea were co-supported. The combination of TiO<sub>2</sub> and urea on the ACF gave high oxidation and reduction of NO. The TiO<sub>2</sub> photocatalyst converted NO into NO<sub>2</sub>, which was immediately passed over urea on the ACF and reduced into harmless N<sub>2</sub>. Humidity seemed to accelerate the desorption of NO<sub>2</sub> from the TiO<sub>2</sub> surface, but did not affect the NO oxidation, indicating that humidity did not interfere with the reaction of NO into N<sub>2</sub>. The ACF system described is potentially very useful for the harmless removal of NO in the atmosphere near the roadside of urban area using natural wind effectively.

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### 1. Introduction

Atmospheric NO<sub>x</sub> in urban areas has markedly decreased after imposing selective catalytic reduction (SCR) for flue gas, three-way catalyst systems for mobile gasoline engines, and diesel particulate filtering (DPF) for diesel engines, to reduce the exhaust NO<sub>x</sub> in addition to lowering the NO<sub>x</sub> from combustion. Nevertheless, some particular areas such as busy intersections where air movement is not sufficient to circulate the atmosphere are highly contaminated with NO<sub>x</sub>, causing health problems to inhabitants of the neighborhood. Large cities and their suburbs are forced to take action to reduce NO<sub>x</sub> in such areas.

The removal of atmospheric NO<sub>x</sub> at room temperature has been proposed using several methods, including photocatalytic oxidation on TiO<sub>2</sub> [1], biological oxidation [2], sorption in soil [3], and adsorption with activated carbon (AC) [4]. However, adsorption of NO must be saturated at a certain level or eluted out in the form of HNO<sub>3</sub>. Special care is necessary when attempting to clean the atmosphere. The maximum amount of air must be in contact with the surface of the catalyst and adsorbent materials to

clean the air. However, the intimate contact inevitably increases the pressure drop of the atmospheric flow, decreasing the flow volume of the atmosphere being cleaned. Larger activity is thus necessary to reduce the amount of adsorbent material required and to improve the efficiency due to the pressure drop. Such large pressure drops require a blower or pump, increasing the cost. Soil sorption may be ruled out for this reason and photocatalytic oxidation requires light. Additionally, NO<sub>2</sub> desorption cannot be allowed to occur, or else the NO<sub>2</sub> concentration in the atmosphere increases by passing the NO containing atmosphere through the photocatalyst, such as TiO<sub>2</sub>, according to the following reaction; NO + (1/2)O<sub>2</sub> → NO<sub>2</sub>. Thin layers of activated carbon fiber (ACF) have the potential to resolve this issue, although higher activity is required to reduce the amount of ACF and to decrease the space required for the installation. Hence, a combinatory cooperation of the catalyst and/or photocatalyst with ACF is required. Also, in these cleaning systems, reducing NO<sub>x</sub> to harmless N<sub>2</sub> that can be liberated directly into the atmosphere is desirable. The previous studies have reported that urea impregnated onto ACF reacts with NO<sub>2</sub> effectively to produce N<sub>2</sub> and H<sub>2</sub>O at room temperature [5–7].

We examined the combination system of TiO<sub>2</sub>, urea, and ACF, to enhance the photocatalytic oxidation of NO in the atmosphere into NO<sub>2</sub> by the TiO<sub>2</sub> photocatalyst, followed by continuous reduction into N<sub>2</sub> and H<sub>2</sub>O by urea on the ACF [8]. A larger volume of NO can

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**Table 1**  
Elemental composition and porosity of ACF samples.

Samples	C (wt.%)	H (wt.%)	N (wt.%)	O (diff) (wt.%)	Ash (wt.%)	$S_{\text{BET}}^a$ (m <sup>2</sup> /g)	$V_{\text{T}}^b$ (cm <sup>3</sup> /g)	$w^c$ (nm)
ACF (as-received)	94.09	0.81	0.25	4.85	0.16	1930	0.95	0.98
ACF (after heat treatment)	97.26	0.32	0.31	2.11	0.54	1568	0.75	0.96

<sup>a</sup> N<sub>2</sub>-BET surface area.

<sup>b</sup> Total pore volume.

<sup>c</sup> Average pore width.

be trapped over ACF than TiO<sub>2</sub> alone due to the large surface area of ACF. Thus, we can expect that once the NO is adsorbed over ACF, it is transferred to TiO<sub>2</sub> for the successive photocatalytic oxidation. At the same time, we can also expect the catalytic oxidation of NO into NO<sub>2</sub> by the ACF itself [9–11]. NO<sub>2</sub> produced by TiO<sub>2</sub> and ACF is an issue for the successful combination of photocatalyst oxidation and reduction by urea on ACF. Although the liberation of NO<sub>2</sub> from the TiO<sub>2</sub> surface was observed, the transfer of NO<sub>2</sub> to urea on ACF must be enhanced through the close contact of TiO<sub>2</sub> and ACF. On the other hand, humidity has been reported to inhibit the oxidation of NO over ACF due to stronger adsorption of H<sub>2</sub>O compared to NO [9,10]. However, humidity does not affect the reaction of NO<sub>2</sub> with urea on ACF [5]. The influence of humidity on the photocatalytic oxidation was also considered in this study. Condensed water over TiO<sub>2</sub> has been reported to elute HNO<sub>3</sub> [12–14].

## 2. Experimental

### 2.1. Materials

Titanium dioxide (TiO<sub>2</sub>; ST-01) powder, quartz wool (fine grade, 2–6 μm), and pitch-based ACF with high surface area (OG-20A-As) were obtained from Ishihara Sangyo Co. Ltd., Tosho Co., and Osaka Gas Co., respectively. ACF heat-treated at 1100 °C for 1 h in an atmosphere of argon was used in this study. Properties of the ACF samples are shown in Table 1.

### 2.2. Sample preparation

The heat-treated ACF was placed into an aqueous solution of urea and stirred for 24 h at room temperature, filtered without washing, and dried at 50 Torr for 1 h in a vacuum oven. Typically, 0.5 g of ACF was placed into 100 mL of aqueous urea solution (0.125–2.0 mol/L) to obtain urea-impregnated ACF (urea/ACF) at different loading amounts. TiO<sub>2</sub> powder was uniformly mixed with the quartz wool carrier with or without impregnated urea using a pestle and mortar, or with ACF carrier with or without impregnated urea.

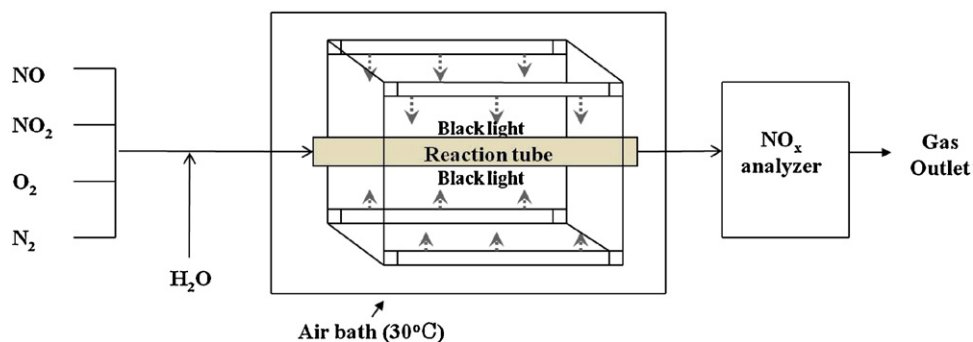
### 2.3. Reactivity measurement

Reaction of NO (or NO<sub>2</sub>) in mixed air composition was performed in a fixed bed flow reactor as shown in Fig. 1. The samples were closely packed into transparent quartz tubes (inner diameter: 12–13 mm, outer diameter: 15 mm, length: 50 cm). The length of the packed samples was 12–24 cm. The composition and flow rate of the NO and O<sub>2</sub>–N<sub>2</sub> mixture (21:79, vol/vol, mL) were adjusted to 50–100 ppm and 100 mL/min, respectively. Gas hourly space velocity (GHSV) was calculated to be about 188–377 h<sup>−1</sup>. The concentration of NO at the inlet and outlet of the reactor was measured continuously using a NO<sub>x</sub> analyzer (ECL-88US; Yanagimoto Co. Ltd.). The reaction tube was irradiated by four black lights (15 W). The distance between the reaction tube and the black light was about 12 or 30 cm.

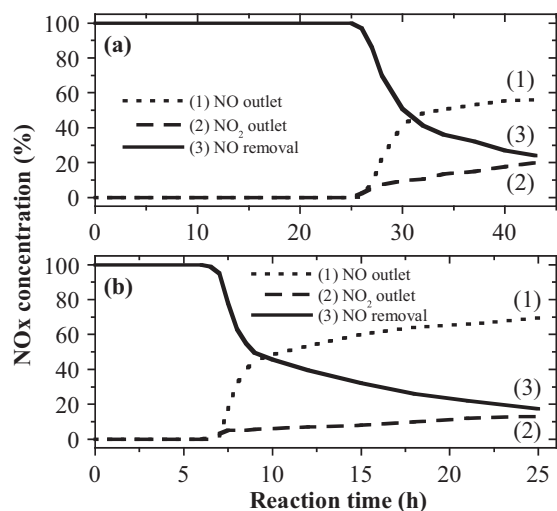
## 3. Results

### 3.1. NO oxidation on TiO<sub>2</sub>

Fig. 2 shows the oxidation of 50 ppm or 100 ppm NO in air under UV irradiation over TiO<sub>2</sub> mixed with quartz wool. NO was stable without UV irradiation (data not shown). Under UV irradiation, NO was oxidized and adsorbed over TiO<sub>2</sub>. No nitric product was detected for a period of time; length of time was strongly dependent upon the inlet NO concentration. NO of 50 ppm and 100 ppm were removed completely for 25 and 6 h, respectively. After these times, NO started to break through, and the outlet concentration increased in both cases. At these breakthrough times, NO<sub>2</sub> began to be detected in the outlet gas the concentration and increased gradually to about 20 and 15%, respectively. These profiles indicated the oxidative adsorption of NO<sub>x</sub>, likely in the form of NO<sub>2</sub>, which had saturated the TiO<sub>2</sub> surface at the time of breakthrough. At this point, the surface NO<sub>2</sub> underwent desorption, while NO removal continued but at a lower efficiency. Finally, NO oxidation into NO<sub>2</sub> became stationary, the NO<sub>2</sub> desorption becoming the rate-limiting step to free the active sites on the catalyst. Photocatalytic oxidation of NO over TiO<sub>2</sub> to produce NO<sub>2</sub> has been reported [12–16], but the continuous liberation of NO<sub>2</sub> is a concern when this kind of photocatalytic oxidation is applied. This photocatalytic reaction,



**Fig. 1.** Schematic picture of the NO oxidation reactor.

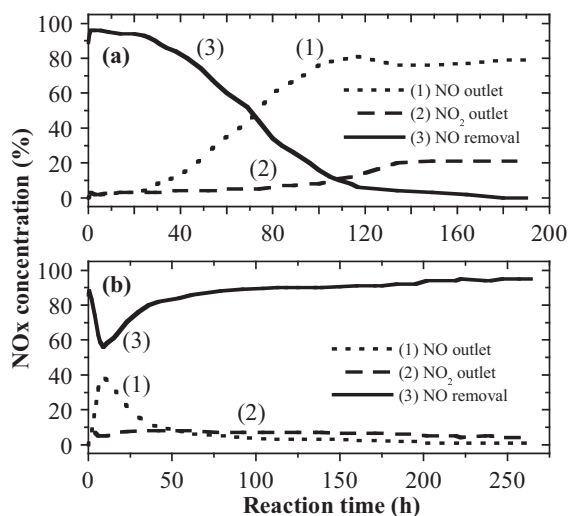


**Fig. 2.** NO conversion over TiO<sub>2</sub> dispersed on quartz wool under UV irradiation. TiO<sub>2</sub>: 0.5 g; RH: 0%. (a) NO: 50 ppm and (b) NO: 100 ppm.

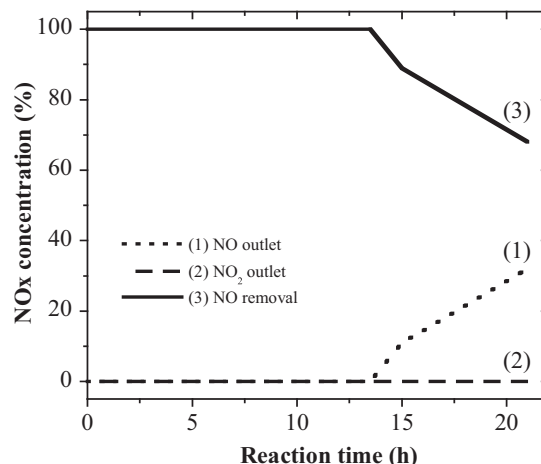
however, is rapid and if an efficient process can be developed to convert the NO<sub>2</sub> into N<sub>2</sub>, it could be used advantageously.

### 3.2. NO reduction under UV irradiation over TiO<sub>2</sub>–urea mixture

Fig. 3 shows the NO removal profiles using UV irradiation over a TiO<sub>2</sub>–urea mixture, varying the urea concentration on quartz wool. The presence of urea reduced the NO<sub>2</sub> produced through the photocatalytic oxidation of NO over TiO<sub>2</sub>. The NO conversion increased for the first 30 min and then remained steady for 20 h using 0.05 g of urea (Fig. 3a). Outlet NO increased very slowly after 20 h to be about 80% after 110 h. NO was removed through the photocatalytic oxidation into NO<sub>2</sub> and its subsequent reduction with urea. The reduction continued until the urea was consumed. Increasing the amount of urea to 0.5 g resulted in a large decrease in the initial conversion (Fig. 3b). This conversion decreased to reach the minimum at 10 h, and the conversion achieved was approximately 95% at 260 h. Both the outlet NO<sub>2</sub> and NO stayed at about 5%. Increasing the amount of urea simply increased the elapsed time of reduction except for the initial drop of the conversion. Urea mixed in large amounts may block off the UV light irradiated to TiO<sub>2</sub>, interrupting



**Fig. 3.** NO conversion over TiO<sub>2</sub>–urea mixture dispersed on quartz wool under UV irradiation. NO: 100 ppm; RH: 0%. (a) Mixture of TiO<sub>2</sub> (0.5 g) and urea (0.05 g) and (b) mixture of TiO<sub>2</sub> (0.5 g) and urea (0.5 g).



**Fig. 4.** NO conversion over TiO<sub>2</sub> mixed with ACF under UV irradiation. NO: 100 ppm; TiO<sub>2</sub>: 0.5 g; ACF: 0.5 g; RH: 0%.

the photocatalytic oxidation. The slow decrease in the conversion before the end of urea consumption may be due to the dependence of NO<sub>2</sub> spillover on the distance from TiO<sub>2</sub> to urea.

### 3.3. NO oxidation over TiO<sub>2</sub>–ACF mixture under UV irradiation

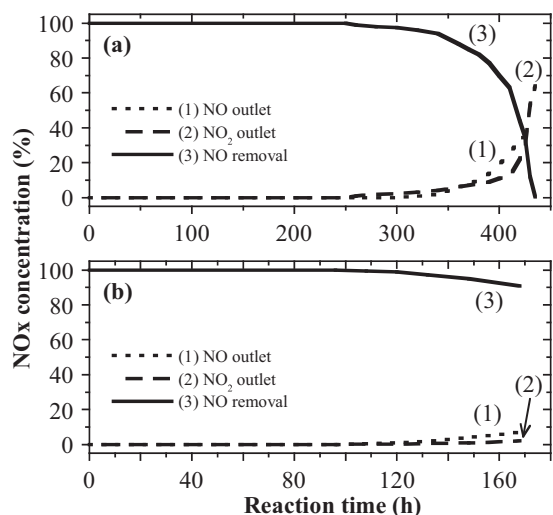
Fig. 4 shows NO oxidation under UV irradiation over a TiO<sub>2</sub>–ACF mixture. NO was completely removed for 13 h without releasing any nitric gases. After the breakthrough, the outlet NO increased gradually to reach approximately 30% after 20 h, while no NO<sub>2</sub> was detected in the outlet gas. The spillover of NO<sub>2</sub> produced on the TiO<sub>2</sub> surface to outlet gas was very slow due to the abundant micropores of ACF providing a large surface area to trap the produced NO<sub>2</sub> from the TiO<sub>2</sub> surface. Comparing the results of Fig. 4 with those of Fig. 2b, ACF was shown to be an excellent trap for spillover NO<sub>2</sub> from the TiO<sub>2</sub> surface, leading to no NO<sub>2</sub> release. Passage of NO<sub>2</sub> from the TiO<sub>2</sub> surface to the ACF micropores to free the active sites should enhance the oxidation over the TiO<sub>2</sub> surface for the longest time.

### 3.4. NO oxidation and reduction over TiO<sub>2</sub>–urea/ACF mixture under UV irradiation

Fig. 5 shows the effects of urea on NO reduction over a TiO<sub>2</sub>–urea/ACF mixture, which was prepared by the impregnation of urea onto the ACF prior to mixing with TiO<sub>2</sub>. Fig. 5a and b shows the changes in the inlet NO concentration (50 ppm and 100 ppm, respectively). In both cases, no NO<sub>2</sub> was detected in the outlet and 100% conversion of NO was achieved over a period of time longer than 250 h or 100 h, respectively. Effective removal of NO was attained by the combination of TiO<sub>2</sub> and the ACF with the impregnated urea. The urea in the vicinity of TiO<sub>2</sub> enhanced the spillover of NO<sub>2</sub>, which was rapidly reduced to N<sub>2</sub>, opening the active site of TiO<sub>2</sub> to provide the higher activity of the photocatalyst.

### 3.5. Reactivity of NO<sub>2</sub> over TiO<sub>2</sub> with/without UV irradiation

Fig. 6 shows the reactivity of NO<sub>2</sub> over TiO<sub>2</sub> without or with UV irradiation. Without the UV irradiation, NO<sub>2</sub> of 100 ppm produced 35% NO for the first 27 h, suggesting the disproportionation [17] of NO<sub>2</sub> into NO and NO<sub>3</sub> on TiO<sub>2</sub>. NO<sub>2</sub> adsorption and NO formation gradually decreased to zero by 50 h and 38 h, respectively, indicating the decrease in disproportionation. Single oxidation leading to adsorption required a slightly longer time to reach zero. Disproportionation requires two molecules of NO<sub>2</sub> in the vicinity; isolated

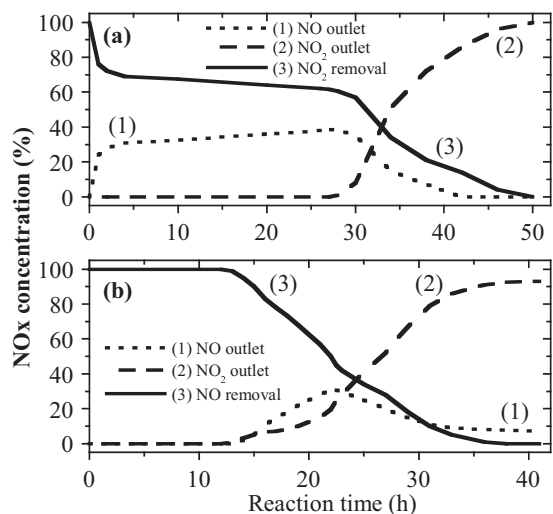


**Fig. 5.** NO conversion over  $\text{TiO}_2$ -urea/ACF mixture under UV irradiation. RH: 0%. (a) NO: 50 ppm;  $\text{TiO}_2$ : 0.5 g; urea: 0.168 g; ACF: 0.5 g and (b) NO: 100 ppm;  $\text{TiO}_2$ : 0.5 g; urea: 0.116 g; ACF: 0.5 g.

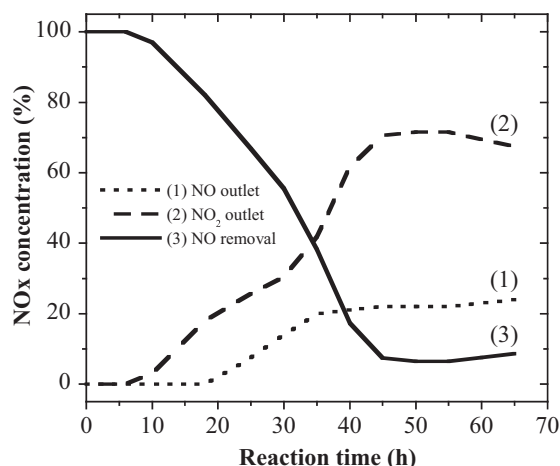
sites cannot perform the disproportionation reaction. UV irradiation accelerated the oxidation of  $\text{NO}_2$  on the single site, and thus no disproportionation was observed until the adsorption started to decrease after 13 h (Fig. 6b). At this point, the NO concentration started to increase in the outlet. Slow disproportionation continued. Note that almost complete removal of  $\text{NO}_2$  continued on  $\text{TiO}_2$  for 27 h and 13 h, without and with UV irradiation, respectively. Disproportionation allows adsorption of one  $\text{NO}_3$  molecule from two  $\text{NO}_2$  molecules with leasing one NO molecule to air, while single oxidation consumes one molecule, saturating the sites more rapidly with less  $\text{NO}_2$ .

### 3.6. Influence of humidity on NO oxidation and reduction with urea

Fig. 7 shows NO oxidation under UV irradiation over  $\text{TiO}_2$  at 50% humidity. Complete removal of NO continued for approximately 6 h. After this point,  $\text{NO}_2$  was detected in the outlet gases, increasing gradually to 70% at 45 h after the reaction initiation. Comparing the reaction without humidity (Fig. 2a) to that of 50% humidity,



**Fig. 6.** The reactivity of  $\text{NO}_2$  over  $\text{TiO}_2$  dispersed on quartz wool without or with UV irradiation.  $\text{NO}_2$ : 100 ppm;  $\text{TiO}_2$ : 0.5 g; RH: 0%. (a) Without UV irradiation and (b) under UV irradiation.



**Fig. 7.** NO oxidation under UV irradiation over  $\text{TiO}_2$  dispersed on quartz wool in humid condition (RH: 50%). NO: 50 ppm;  $\text{TiO}_2$ : 0.5 g.

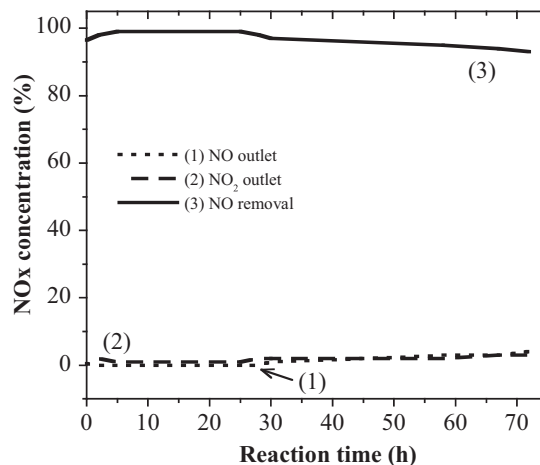
the period of complete removal was markedly shortened with 50% humidity, while  $\text{NO}_2$  formation was enhanced; humidity appeared to accelerate the desorption of  $\text{NO}_2$  produced from NO over the  $\text{TiO}_2$ , but not the elution of  $\text{NO}_3$  in the form of  $\text{HNO}_3$ .

Fig. 8 shows the reactivity of NO at 50% humidity over  $\text{TiO}_2$  with urea supported on ACF, a  $\text{TiO}_2$ -urea/ACF mixture. The results showed that the removal of 95–100% NO continued for 70 h without producing any nitric gases. Comparing the results of Fig. 8 to those of Fig. 5a under the same condition except for humidity, the same reactivity of NO was obtained, indicating that humidity had a very small influence on the removal of NO. The  $\text{NO}_2$  trap of  $\text{TiO}_2$  was certainly inhibited by humidity, but NO oxidation on  $\text{TiO}_2$  were not affected. Together with the accelerated  $\text{NO}_2$  spillover, overall NO removal efficiency was not interfered by the humidity.

## 4. Discussion

### 4.1. Reactivity of NO over $\text{TiO}_2$

Little NO reaction over  $\text{TiO}_2$  occurs without UV irradiation, which greatly enhances NO oxidation over  $\text{TiO}_2$ , and the oxidized products stay over the surface of  $\text{TiO}_2$  until the surface is saturated (Fig. 2). After the saturation, some  $\text{NO}_2$  is liberated in the gas phase from the surface. The photocatalytic oxidation of NO into



**Fig. 8.** NO conversion over  $\text{TiO}_2$ -urea/ACF mixture under UV irradiation in humid condition (RH: 50%). NO: 50 ppm;  $\text{TiO}_2$ : 0.5 g; urea: 0.195 g; ACF: 0.5 g.

NO<sub>2</sub> appears to continue after the saturation of adsorbed NO<sub>2</sub> in an almost first-order reaction.

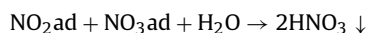
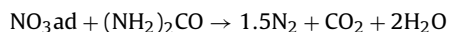
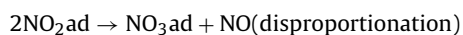
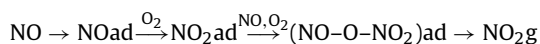
TiO<sub>2</sub> has been applied to remove NO in the atmosphere. It removes NO through oxidative adsorption, but the liberation of produce NO<sub>2</sub> through the photocatalytic oxidation of NO must take place after the saturation of NO<sub>2</sub> adsorption. Thus, an effective NO removal should be designed by trapping and/or reducing the NO<sub>2</sub> produced.

#### 4.2. Combination of TiO<sub>2</sub> with urea or urea-impregnated ACF

NO<sub>2</sub> from NO oxidized over TiO<sub>2</sub> can be trapped or reduced by coexisting reductive adsorbents or reactive reductants such as urea. Hence, we can design an effective way for reductive NO removal at room temperature for a much longer time, depending upon the adsorption capacity or amount of reductant urea used, increasing the time over that of TiO<sub>2</sub> alone.

An adsorbent or reductant in contact or located in the vicinity of TiO<sub>2</sub> appears to accelerate NO<sub>2</sub> desorption from TiO<sub>2</sub> (cf. Figs. 2b and 4). A spillover mechanism occurs with TiO<sub>2</sub> and accelerates the NO oxidation, enhancing regeneration of the active sites on the TiO<sub>2</sub> surface. The spillover mechanism is also valuable for the combination of TiO<sub>2</sub> and the adsorbent or the reductant, improving efficiency.

The present study applied ACF and urea separately and in combination with TiO<sub>2</sub> to investigate their roles (Figs. 3–5). ACF can adsorb the spillover NO<sub>2</sub> in the form of NO<sub>3</sub>, until adsorption is saturated [5,17]. Higher NO of combined system expected compared to that of TiO<sub>2</sub> alone. ACF can also oxidize NO into NO<sub>2</sub> to be adsorbed [9–11]. Thus, the activity is summed. TiO<sub>2</sub> is active only under irradiation, and mixing TiO<sub>2</sub> with ACF may interfere with the irradiation onto TiO<sub>2</sub>; it would be suitable to place TiO<sub>2</sub> in front of the ACF or in the vicinity of the reactor wall above the ACF to reduce these interferences. NO<sub>3</sub> on ACF can be eluted in the form of HNO<sub>3</sub> to free-up the adsorption sites of ACF [17]. Urea can be a reductant against the spillover NO<sub>2</sub>, and it can be mixed directly with TiO<sub>2</sub> or supported on ACF. Possible reactions are expressed as follows [5,6,11].



Here, there is a possibility that NH<sub>3</sub> produced by photocatalytic decompositions of urea also participates underlying reactions with NO and NO<sub>2</sub>. Urea in aqueous solution has been reported to be decomposed over TiO<sub>2</sub> under the UV irradiation [18], and NH<sub>3</sub> can react with NO into N<sub>2</sub> over TiO<sub>2</sub> under the UV irradiation [19–21]. The produced NH<sub>3</sub> could be also consumed by reactions with NO and NO<sub>2</sub> on ACF [6].

When urea is supported on both TiO<sub>2</sub> and ACF, more urea can be charged at a time in the reactor. However, some of the active sites over TiO<sub>2</sub> must be covered by urea; if the urea amount increases, the TiO<sub>2</sub> becomes less active to NO. Powder mixing of urea and TiO<sub>2</sub> may create the same problem and hence urea highly dispersed on ACF is the best combination to mix with TiO<sub>2</sub>.

The NO<sub>2</sub> produced over TiO<sub>2</sub> can spill over to the ACF surface. NO<sub>2</sub> spillover to the adsorbent will stay adsorbed or further spill over to the urea on the ACF surface. Thus, the complete NO removal

becomes very efficient when combining TiO<sub>2</sub> with urea on ACF (Fig. 5).

#### 4.3. Influence of humidity

Stronger adsorption of water than NO is recognized to inhibit NO oxidation over ACF [9,10]. In addition, water will extend the time of complete removal over TiO<sub>2</sub> under irradiation through the liberation of NO<sub>2</sub>. An enhancement of NO<sub>2</sub> desorption accelerates the oxidation through the rapid regeneration of the active sites of TiO<sub>2</sub>, and thus, total NO oxidation is not altered by humidity. Desorbed NO<sub>2</sub> is trapped and/or reduced by ACF, urea, or urea-supported ACF. Hence, inhibition by humidity does not interfere with the NO removal by TiO<sub>2</sub> combined with urea on ACF, although ACF activity for the NO oxidation may be limited.

### 5. Conclusion

The combination of TiO<sub>2</sub> with urea over ACF provided the NO reductive removal at room temperature, which was not affected by humidity. Urea was available in the combined form of ACF, but UV light (daylight) was necessary. Therefore, air pollution close to busy roads during the day may be addressed with this type of system. At night, less traffic will create less NO, which will be removed by ACF, and ACF is also able to oxidize NO without light. Urea can be supplied over ACF when needed. Thus, the present combination can be utilized for the harmless removal of NO in the atmosphere. Natural wind or wind provoked by moving traffic can direct NO through the system described, cleaning the local atmosphere.

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